

The Possibility of Measuring Variations in the Intensity of Worldwide Lead Smelting During Medieval and Ancient Times Using Lead Aerosol Deposits in Polar Snow Strata

著者	MUROZUMI Masayo, CHOW Tsaihwa J., PATTERSON C.C.
journal or publication title	Memoirs of the Muroran Institute of Technology. Science and engineering
volume	6
number	3
page range	733-742
year	1969-07-15
URL	http://hdl.handle.net/10258/3458

The Possibility of Measuring Variations in the Intensity of Worldwide Lead Smelting During Medieval and Ancient Times Using Lead Aerosol Deposits in Polar Snow Strata

M. Murozumi*, Tsaihwa J. Chow**
and C. C. Patterson***

Abstract

When lead is smelted in blast furnaces, hot gases in the furnaces carry a considerable fraction of the lead up into the atmosphere in the form of fine particles. Although the amount lost is modified by smelting conditions and attempts to recover the fume, an approximate value for the fraction lost might be about 1%. These particles are mostly removed from the atmosphere by rain or snow. Meteorological conditions average out over a year, and precipitation mechanisms are highly effective in removing suspended aerosols, so that total concentrations of lead particles in the atmosphere respond within about a year to changes in smelting activities and an average of a year's accumulated precipitation will show little variation from year to year if smelting remains constant, but will change from year to year if the intensity of smelting changes. In recent decades, an additional source of lead in the atmosphere has been the burning of leaded gasoline. The fraction of lead produced each year which is burned in automotive and aviation fuels increased from zero in 1923 to 15% by 1955. In contrast to the low yield from smelter fumes, about 75% of lead in gasolines is converted to long-lived atmospheric aerosols after combustion, so that there has been a recent additional increase in the concentrations of lead in the atmosphere from this new source. As shown in Fig. 1, a record of the increase in lead content of the atmosphere is preserved as progressively younger and dirtier layers of snow in the polar regions of the earth.

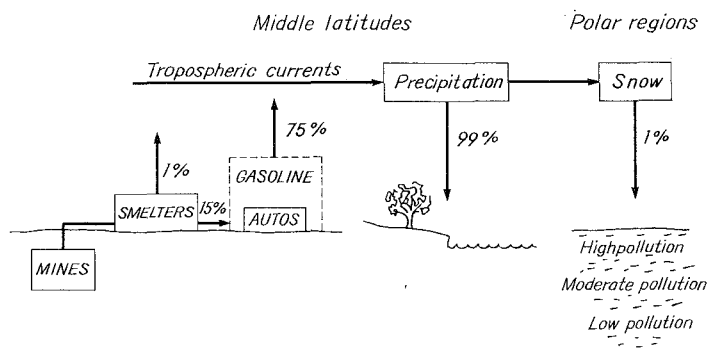


Fig. 1. Industrial lead cycle in the atmosphere.
Percentages given are crude estimates.

* 室住正世 Muroran Institute of Technology, Muroran, Hokkaido, Japan.

** Scripps Institution of Oceanography, University of California at San Diego, California.

*** Division of Geological Sciences, California Institute of Technology, Pasadena, California.

Recently, M. Murozumi, Tsaihwa J. Chow, and C. C. Patterson measured the concentrations of lead in the upper two centuries of snow layers near the North and South Poles¹⁾. They detected a large decrease in lead content going down to the older snows near the North Pole, but the lead contents of the snows near the South Pole were so small only a slight decrease was noted. They also showed that there were no similar changes in the amounts of rock dust and sea salts with time, and that the concentrations of these substances were too low to account for the amounts of lead present. They were thus able to detect recent lead pollution of the atmosphere and distinguish between relatively unpolluted southern hemispheric air and strongly polluted northern hemispheric air. The advantages of going to the thick ice shields in polar regions are that the yearly accumulations there are slight enough so that hundreds of years are accessible and the rate of horizontal flow of compressed snow and ice is insufficient to distort and mix hundreds of yearly layers (the disadvantages are that the pollution effect is greatly diminished, and collection of the snow samples there is difficult and costly). These findings suggest that it may be possible to examine frozen records of ancient atmospheres for changes in the intensity of industrial activity. Lead is particularly suitable for this purpose because in past millenia one of the fundamental indices of economy, silver, was obtained by smelting it out of lead. For each ton of silver produced some 400 tons of lead metal, on the average, were first smelted from ores and then cupelled, or oxidized, in a separate operation to yield the eagerly sought after silver which is more difficult to oxidize. In ancient times uses were gradually discovered for the enormous masses of pure lead that were made available by this operation, and thus was born the industrial utilization of lead. Lead metal was easily recovered from the oxide by simply smelting it with charcoal.

The reconstruction of world silver production and, as a corollary, world lead production, in ancient times would be of considerable interest to the economic historians. In a very approximate manner this can be done from evidence based on slag heaps whose sizes and ages have been estimated. The solid curve in Figure 2 shows the approximate production of silver in the world since silver was first smelted in northeastern Turkey 4,600 years ago²⁾. This curve also expresses very well (but in different units) the approximate world production of lead, except for the period after the Industrial Revolution. The 400 to 1 relationship does not hold very well between lead and silver during that last interval, for, in fact, silver production leveled off at about 6000 tons per year after 1880, while lead production continued to climb, as shown by the dotted extension, to some 2,000,000 tons per year at present.

1) Discussed at the 60th Annual Meeting of the Air Pollution Control Association, Cleveland, Ohio, June 11-16, 1967: "Changes in Concentrations of Common Lead in North Polar Snows with Time." M. Murozumi, T. J. Chow and C. C. Patterson.

2) Preliminary figures. A full discussion and evaluation of these data is being written and will be published. (*Geochimica Cosmochimica Acta* Vol. 10. 1969)

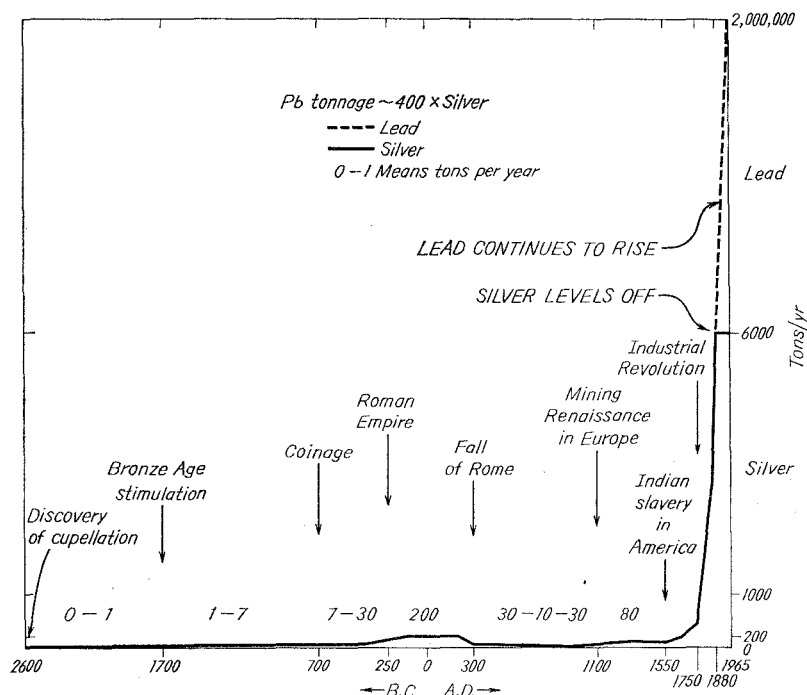


Fig. 2. Total world silver and lead production since the earliest times. Figures are preliminary.

Considering what has been discovered about the variation of lead in polar snow strata, would it be possible to check the magnitude of silver-lead production during the time of the Roman Empire by actual measurement? Also, would it be possible determine the time of minimum production during the Medieval period?

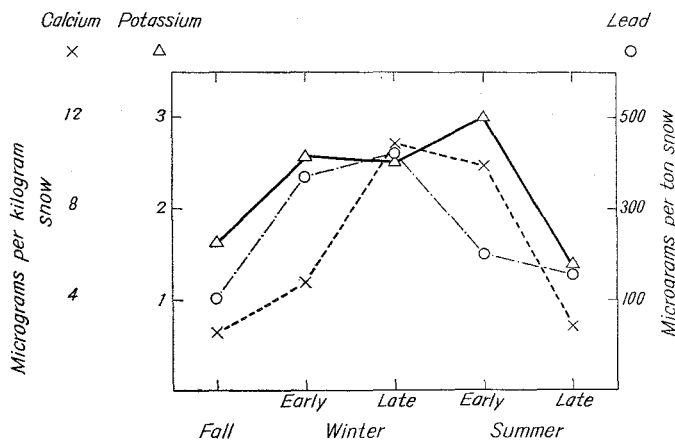


Fig. 3. Seasonal variation in chemical composition of snow at 80 km ESE of Camp Century, North Greenland (76°50' N 58°30' W).

It seems feasible, but further development of present techniques would be necessary. The data already collected can be used to show how this could be done.

Figure 3 shows, near the North Pole, the seasonal variation of calcium, potassium, and lead concentrations in a single year's accumulation of snow found by Murozumi, Chow and Patterson. Most of the calcium and potassium came from clay dusts. It can be seen that in the mid-summer and fall, the concentrations of aerosols were low, while in the winter and early summer, they were high. These large variations, which are a function of meteorological conditions, can be smoothed out by mixing into a single sample snow accumulated during a period of three or four years. Unfortunately Murozumi et al. were unaware of this effect and the year to year samples which they collected and analysed each spanned were mixtures of about one and a half years accumulation which accentuated, rather than smoothed, this seasonal effect.

Figure 4 shows the concentration of sodium found in the snow as a function of time which at this location is largely derived from sea salts. It can be seen that for a span of 200 years there is no systematic increase of salt. Some of the variation is probably due to the samples at different time levels having different proportions of autumn and winter snows in them because each sample, covering about 11/2 years, was taken with a stratigraphic uncertainty greater than that interval. It will be noted that the oldest sample, dated at about 800 BC with

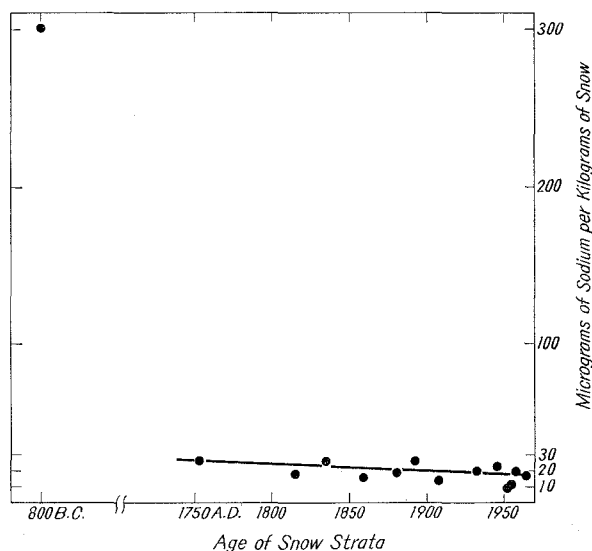


Fig. 4. Year to year variation of sodium in snow at Camp Century, North Greenland ($76^{\circ}10' \text{ N } 61^{\circ}08' \text{ W}$) (1753 AD to 1946 AD), and at 80 km ESE of Camp Century (1952 to 1965). High value is from ancient ice at west edge of shield near Camp Tuto (32 km E of Thule, Greenland). Virtually all of the sodium in all samples is derived from sea salts, not clay dusts.

C¹⁴³⁾ contains very much greater amounts of salt. This is because all the samples except that one were taken from locations in the interior of the Greenland ice sheet, where salt and dust from local seas and shores do not tend to penetrate, but the old sample was taken from a horizontal tunnel drilled into the edge of the ice sheet near the sea and shore, and it came from material highly contaminated with locally derived salts and dusts.

Figure 5 shows that calcium, representing clay dusts, is also affected by the improper sampling. The dust content clearly did not change with time at the interior location, although the old ice sample taken from the shore location was more dusty.

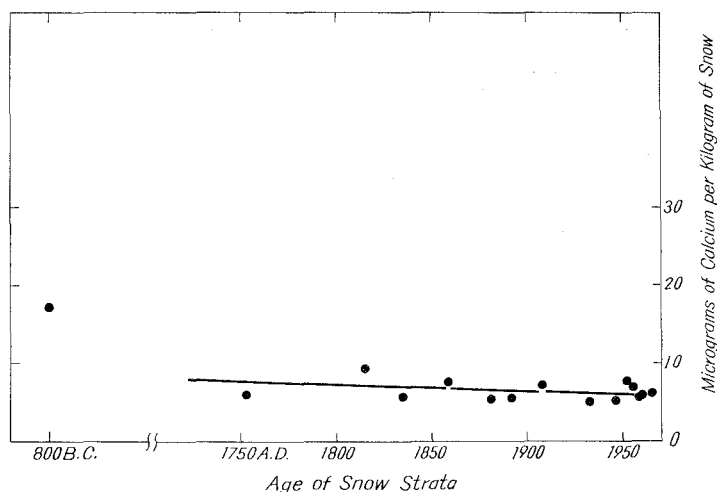


Fig. 5. Year to year variation of calcium in snow at Camp Tuto, Camp Century, and 80 km ESE of Camp Century. Most of the calcium is derived from clay dusts.

Figure 6 shows that the variation of lead in north polar snows increases dramatically with time. We also note that the salty millenia old ice contains the smallest amount of lead. The lead concentration observed in it is within a factor of three of that naturally expected from the salts and dusts present (the extra amount probably originates from the plastic drums and bottles). We would therefore expect 800 BC old snow from the interior to have a lower natural lead content, corresponding to its lower dust content. This would be less than one unit on the scale shown, or less than one part per million \times million of snow. The large scatters of the points from a smooth curve do not reflect year to year variations. They result from a difference in proportions of autumn and winter

3) H. Oeschger, B. Alder, H. Loosli, C. Langway and A. Renaud "Radio Carbon Dating of Ice", *Earth and Planetary Science Letters* 1, 194 (1966). Our sample is from near "location 1". Considering the much older age of "location 2", our sample may be older, rather than younger, than 800 BC.

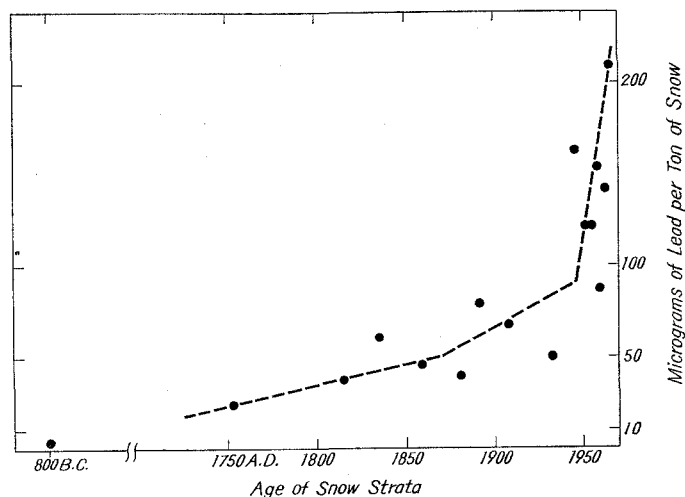


Fig. 6. Year to year variation of lead in snow at Camp Tuto, Camp Century, and 80 km ESE of Camp Century. Lead from natural sources is insignificant in all of these samples. Most of the lead assigned to the 2800 year old sample is probably contamination from industrial lead on the walls of drums and bottles, and was never in the snow. Nearly all of the lead assigned to the 1753 sample is industrial smelter lead actually in the snow. Snow from the Antarctic has assigned lead concentrations similar to the low value found for the 5000 year old Greenland sample.

layers in the samples which covered somewhat more than a year. For this reason it is not clear whether the observed lead curve faithfully reproduces the world lead production curve. Roughly, lead in north polar snow appears to increase by a factor of about four after 1750 and before 1940. After about 1940, there seems to be a sharp, additional increase by another factor of two or three. This is about what we might expect from the known increase of lead smelter production during the Industrial Revolution and from the known increase in burning of leaded automotive fuels during recent decades. Certainly, the data could be greatly improved by repeating the experiment using care to mix snow from about three years accumulation at each dated level.

This information only covers the period since the Industrial Revolution, however. Referring back to Figure 2, it can be seen that in approximate terms the level of lead production in Roman times was about equal to the level at the start of the Industrial Revolution boom in 1750 (lead lagged behind silver in 1750 because a lot of silver was then being taken from non-lead ores, so the silver curve in Figure 2 lies somewhat above a lead curve for that time). This means that the 1950 lead point in Figure 6 should correspond to what could be observed for a Roman lead point in ancient times. The lead value at 1750 is more than order of magnitude above the natural lead content of the snow, so there should be plenty of room for a Roman production peak to appear if it existed. If lead

production during Medieval times were an order of magnitude less than production during Roman times, however, it would be difficult to detect a two or three fold minimum during the Medieval period, since it would probably lie close to natural lead concentrations according to present analytical techniques.

An experiment designed to check by actual measurement the silver production or industrial activity in Roman and Medieval times would consist of three phases: the development of analytical techniques, the digging of a shaft, and the collection of samples.

At the present time the levels of lead contamination in laboratory analytical procedures are too high, but they can be reduced. The sample size is of the order of 50 liters of water. Four to six samples of this size are needed at each dated level for a proper evaluation of the lead concentration. For Roman times a 50 liter melted snow sample from North Greenland would contain only 0.6 micrograms of lead. Before analysis each sample is melted in a separate 30 gallon plastic drum and shipped from the collection site to the laboratory in a 13 gallon plastic bottle. Although in past experiments these containers were cleaned in vats of nitric acid, rinsed with pure water, filled with pure argon to displace lead contaminated air and sealed in plastic bags equipped with breathing filters, they were first shipped from the factory to the laboratory in the midst of auto traffic and were each thereby sprayed, literally, with thousands of micrograms of lead before they were cleaned. Upon evaluating the data it has become apparent that these very large containers, first contaminated and then carefully cleaned, apparently contributed about 0.05 micrograms of lead to each sample, which is too much, compared to that in Roman time samples, for accurate measurement. By collecting the plastic containers at the factory as they come off the production line and sealing them in plastic bags for shipment to the laboratory that source of contamination could be eliminated. At the present time, about 0.1 microgram of lead contamination is added to a 50 liter sample during analysis. The various sources and magnitudes of this contamination are now known (mainly reagents) and promising methods for reducing it by a factor of ten have been proposed. Although it has not yet been done, it is reasonable to suppose that techniques could be developed for the collecting, processing, and analysis of 50 liters of ice melt water with a total contamination of about 0.01 micrograms of lead. For Medieval times, 50 liter snow melt samples from the interior of North Greenland should contain about 0.05 micrograms of industrial lead, which means that measurement capability for the lowest expected concentrations should be above contamination background, providing suitable conditions for reasonably accurate measurements.

The necessarily large size of the samples requires that the ice be mined out in the form of large blocks from a shaft. In the previously sampled Arctic location, the inclined shaft was 1000 feet long and 300 feet deep, while it was 300 feet long and 150 feet deep at the Antarctic location. The shafts were driven with electric chainsaws and electric hoists. Samples were taken from the faces

of short, horizontal adits driven into the walls of the shafts. To prevent contamination, the investigators, at the time of collecting the blocks, were encased in plastic suits and gloves and worked with teflon handled, stainless steel tools that had been cleaned in nitric acid. The freshly removed ice blocks were exposed only a few moments before being sealed in plastic drums. They were melted on electrically heated baths and syphons transferred the water to large bottles. The shafts extended through about 200 annual snow layers. The difference in shaft depths was due to the difference in rates of snow accumulation at the two locations.

A section of more than 2000 annual layers of snow could be sampled by a shaft 1000 feet deep in the north Greenland icesheet near the central interior where snow accumulation is minimal. A 6 foot diameter vertical shaft could be rapidly excavated with a steam drill, which is simply a large heater, or ice melter, fed by steam. Snow shelves in polar regions become impermeable a short distance down, and as the ice shaft filled with melt-water it could be pumped out with an electric pump which followed the heater down. The major requirements would include: a head-frame with attached pulleys, electric winch, and drums capable of handling a five ton load for a length of 1500 feet; generators capable of delivering 100 kW with accessory transformers and transmission lines; several large diesel fuel bladders and accessory pumping equipment; a diesel steam generator; a diesel snow melter with auxiliary storage tank and tractor skip loader; several thousand feet of high pressure, flexible, linked, steam hose plus several thousand feet of high pressure, linked, water hose capable of withstanding a pressure of 1000 psi; several thousand feet of low resistance electric cable; hut enclosure for the head frame assembly, hut enclosure for the generator and snow melter assembly; subsistence and communication units for six working plus four emergency men. After the shaft had been dug, an elevator would be installed on the head frame in place of the steam melter, and the shaft would be wired for power. Short, horizontal adits would be excavated from the walls of the shaft with electric chain saws at appropriate levels. The debris removed by this operation could be dumped into a previously prepared, bell-shaped sump at the bottom of the shaft which had been melted and pumped out when the shaft was dug if it was decided that this would not set up unduly hazardous stresses. If it would be too hazardous then the debris from the side adits would have to be hoisted out which would require additional time. In the sample collecting stage the following year, a laboratory hut would be installed, the ice blocks would be collected, melted, and aliquoted into bottles. It would be difficult to dig the shaft and collect the samples in one season. Even though the work would be within areas unexposed to storms, it might be too exhausting and tedious to be carried out by a wintering-over party. The additional hazards of such an operation might not be balanced by a sufficient diminution of the wall closure hazard. The shafts and adits could be dug in one season and samples from thirty to forty locations could be taken the following summer.

Wall closure above an 800 foot depth might not exceed 20% in a year.

Below that depth, wall closure could be compensated for by enlarging the shaft diameter below that level initially, anticipating about 50% closure within 15 months. For the small void volumes and rounded cross-sections involved, it seems likely that only plastic flow closure without rupture would ensue. Some consideration might be given to the shape of adits that would avoid concentration of stresses and spalling.

The number of required air flights would be small. Operating from Thule, round trip air time for a ski-equipped C-130 to the shaft site would not exceed four hours, allowing 1 hour for unloading and pre-take-off runway packing runs. This short weather prediction time should permit an adequate number of supply flights to be tightly bunched early in the season. In the first season the freight flights might consist of four to bring in the huts plus supplies, two for fuel, and two for auxiliary equipment. In the second season the flights might consist of one for subsistence and personnel, two for container delivery, two for water sample pick-up, and two for equipment retrieval. Much material would be abandoned. The skip-loader might be used to prepare the runway, but it is likely that the expense of jato takeoffs would be required in most instances. The cost of the operation, excluding air transportation and some borrowed major equipment which would include both an electric and a steam generator, winches, huts, subsistence and communication equipment, and vehicles, might come to \$ 200,000 for supplies and salaries for analytical development, collecting, and analysis. The time involved would amount to about two years for development, two years for collecting, and two years for analysis. Time and costs must be provided for in the development of the head-frame, steam melter, elevator, water pump linkages, and removable cable shackles used for the attachment of water, steam, and electric lines to the hoist cable. Although this appears to be a rather extensive operation for one experiment, it could be coupled with several congruent ones.

There are other substances besides lead which might be used as atmospheric indicators of the intensity of industrial activity in medieval and ancient times. Vanadium is one. Like lead, it is a rare element and does not occur naturally to any great extent in air, but it is concentrated in the ash of coal and other carbonaceous fuels. It is virtually certain that the vanadium content of snows would reflect the increase which has occurred in the rate of coal burning. Elements such as iron would record the increase of iron smelter production, but the natural iron content of the atmosphere is high because it is abundant in clay dusts, and the natural iron background in snow might be too high. On the other hand, copper might be a good possibility. It could be measured by neutron activation. Murozumi, et al., used very large volumes of water for their samples, and upon melting their samples in large, separate, very clean, white drums, they observed faint, dark, carbonaceous rings where the water surface had been, whose intensity faded out as the ages of the snow layers from which samples were taken increased to three or four decades. It may be that a sensitive chromatographic

technique could be developed which would detect an organic atmospheric constituent of burned fossil fuels.

A number of physical property studies of ice under extreme pressures, previously impossible with coring techniques, could be carried out. Wintering over parties could make use of the surface site for more typical studies.

In any case, it seems perfectly feasible to measure relative changes in silver production and industrial activity at various times several thousand years ago. The lead experiments that have already been carried out and cited above were supported in several seasons at Camp Tuto and Camp Century, Greenland, as part of the operations of the U.S. Cold Regions Research and Engineering Laboratory at Hanover, New Hampshire. Laboratory work and supplies were funded by the U.S. Atomic Energy Commission and the U.S. Public Health Service. Lead measurements at Byrd Station in the Antarctic were funded by the Antarctic Research Program of the National Science Foundation and the U.S. Atomic Energy Commission.

(Read before "at the International Conference on the Application of Science to Medieval Archaeology", October 1967, Los Angeles.)

(Received April. 28, 1969)